

# Effects of Cu in CdS/CdTe solar cells studied with patterned doping and spatially resolved luminescence

S. D. Feldman,<sup>a)</sup> R. T. Collins, V. Kaydanov, and T. R. Ohno  
*Department of Physics, Colorado School of Mines, Golden, Colorado 80401*

(Received 5 April 2004; accepted 29 June 2004)

CdS/CdTe solar cells were nonuniformly doped at the backsurface of the CdTe with Cu evaporated through a shadow mask. Spatially resolved electroluminescence measurements showed strong correlation of emission intensity with the Cu pattern for all photon energies. Photoluminescence (PL) measurements performed on the exact same region showed no correlation with the Cu pattern when integrated over all energies. However, lower energy PL (located in a broad defect-related band) was slightly more intense in Cu-doped regions, whereas the intensity of PL from shallower states was slightly greater in undoped regions. These small differences in spectra were discernable only with the patterned doping and spatially resolved characterization used here. © 2004 American Institute of Physics. [DOI: 10.1063/1.1787596]

Due to its direct,  $\sim 1.5$  eV, room temperature, band gap,<sup>1</sup> CdTe is a material almost ideally suited for thin film photovoltaics. Cell efficiencies up to 16.5%<sup>2</sup> have been demonstrated in polycrystalline devices. Low-cost solar cells can be constructed with films only a few  $\mu\text{m}$  thick. A primary focus of CdTe solar cell research involves the backcontact. In almost all devices, the backcontact is itself a diode due to the high work function of CdTe. Generally Cu is added as a *p*-type dopant to minimize the potential barrier that forms between the metal and CdTe. The application of Cu to improve CdTe performance, particularly to reduce backcontact series resistance ( $R_s$ ), is crucial to obtaining high efficiency devices as shown by its presence in record CdTe solar cells. At the same time, Cu is suspected to have some detrimental effects including decreased stability in CdTe devices.

In this study, we have chosen to investigate Cu within polycrystalline devices because they represent the state of the art in CdTe photovoltaics<sup>2</sup> and because postdeposition processing (such as  $\text{CdCl}_2$  treatment) greatly affects device performance<sup>3</sup> and defect concentrations.<sup>4</sup> The defects Cu can form include Cu substitutions onto a Cd site ( $\text{Cu}_{\text{Cd}}$ ), Cu interstitials ( $\text{Cu}_i$ ), and various complexes with both native and non-native defects formed during processing. Previously, we have tried to isolate Cu effects by fabricating nominally identical devices with and without intentionally adding Cu. However, the interpretation of these experiments is complicated by the fact that Cu is present in most CdTe thin films, even when it is not intentionally added.<sup>5</sup> Furthermore, identically processed cells, even nearest neighbors from the same substrate, suffer from nonuniformity issues,<sup>6</sup> resulting in different characteristics, making it even more difficult to uniquely isolate the effects of Cu. In this study, we avoid many of these problems by creating a well-defined array of Cu doped and undoped regions in a single cell. Spatially resolved electro-optical characterization techniques then allow Cu doped and undoped regions of the exact same cell to be studied.

For the devices studied in this letter, the TCO, vapor transport CdS and CdTe layers, as well as the  $\text{CdCl}_2$  treatment (annealing) were processed by First Solar, LLC as in

Ref. 7. Postprocessing and backcontact application was conducted at the Colorado School of Mines. The material is first etched for 30 s with a 1% Br methanol solution. In a typical process, 30 Å of Cu is then evaporated over the entire surface of the substrate. As discussed in the following, it is this step that we modified in our test devices. After annealing in nitrogen at 200 °C for 7 min, excess Cu is removed with a 30 s dip in a 0.5% Br: methanol solution. Finally, 500 Å of Au is evaporated to complete the backcontact. The Au pad, 1.6 mm in diameter, defines the cell size.

To introduce a well-defined array of Cu-rich regions into a cell for this study, one modification was made. Figure 1(a) schematically demonstrates deposition of this array. Instead of depositing Cu over the entire backsurface of the CdTe, Cu was evaporated through a shadow mask with circular holes  $\sim 150$   $\mu\text{m}$  in diameter. The result is a cell with a Au backcontact and with many circular Cu-rich regions (dots) underneath, occupying  $\sim 15\%$  of the area of the cell.

Electroluminescence (EL) and photoluminescence (PL) were employed as probes of material properties. While both techniques rely upon the detection of photons emitted from recombining excess carriers, the method of carrier injection differs. With EL, excess minority carriers are injected elec-

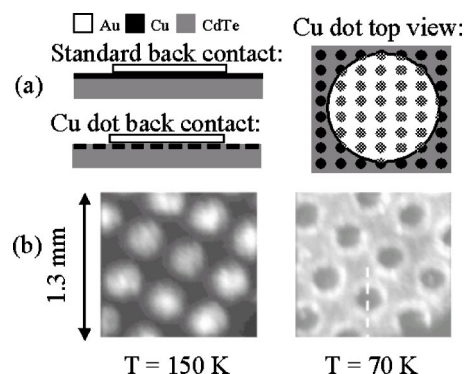


FIG. 1. (a) Schematic representation of patterned Cu doping. (b) EL image from Cu dot cell at 150 and 70 K. Except for the edge of the cell in the lower right-hand corner of the image, EL intensity from black areas of the images was not zero, but was less than half the intensity of brighter areas. The dashed line in the 70 K image indicates the location of line scans in Fig. 2.

<sup>a)</sup>Electronic mail: sfeldman@mines.edu

trically through the front- and backcontacts whose electrical properties profoundly influence EL. In PL carriers are injected optically (in this case with a 1.96 eV helium–neon laser) and are to first order unaffected by contact properties under the open circuit conditions used here. EL and PL measurements were performed from the glass side of the cell and under the Au backcontact. However, the lower right corner of the images in Fig. 1(b) is not under backcontact and shows no EL emission.

To obtain spatial images of EL intensity, the cell was forward biased to obtain an average current density of 25 mA/cm<sup>2</sup> (approximately the magnitude of current during device operation) and the resultant EL was focused onto the entrance slit of an Acton 300i spectrometer with a Princeton Instruments Spec-10:100BR CCD array detector. The spectrometer had two gratings and a mirror mounted on a rotating turret. Using the mirror, and opening the slit to 2 mm, spatial images of EL as in Fig. 1(b) were obtained. For spectral resolution, a grating is rotated into position and the slit width is reduced. The signal that passes through the spectrometer is dispersed onto the CCD detector. Because the detector is a two-dimensional array, spectrographic information is obtained along the horizontal axis of the CCD, while spatial information is obtained along the vertical axis. With PL, the laser beam was focused with a cylindrical lens such that the beam was roughly uniform (within a factor of 3) over the area of the cell imaged through the slit. The average laser power was  $\sim 20$  mW/cm<sup>2</sup> ( $\sim 0.2$  suns), similar to normal operating conditions. PL data were normalized to the laser power.

EL emission correlated well with the location of the Cu dots as shown by the images in Fig. 1(b). From room temperature down to  $\sim 100$  K, EL intensity was up to an order of magnitude greater on the Cu dots. This result is consistent with Cu reducing backcontact  $R_s$ . Below 100 K, the EL pattern inverted, with the intensity from non-Cu (undoped) regions several times that of Cu doped regions. A possible explanation for this inversion involves changes in the defects responsible for transport. Assuming that Cu incorporates itself primarily as  $\text{Cu}_{\text{Cd}}$  for these processing conditions, Cu regions should contain fewer  $V_{\text{Cd}}$  defects as Cu occupies the vacant Cd site. Theoretical work by Wei and Zang places  $\text{Cu}_{\text{Cd}}$  as a deep acceptor at  $E_v + 0.22$  eV above the valence band, whereas  $V_{\text{Cd}}$  is shallower at  $E_v + 0.13$  eV.<sup>8</sup> As the temperature drops near 100 K, the  $\text{Cu}_{\text{Cd}}$  levels freeze out, creating a higher  $R_s$  in Cu doped regions than in undoped regions where shallower defects (such as  $V_{\text{Cd}}$ ) are still electrically active. Below 100 K, undoped regions then have the lower  $R_s$ , draw more current, and therefore show brighter EL emission. Because the signal is greater at lower temperatures, all comparisons between EL and PL were made with the data taken at 70 K. It is important to note that cells processed with a different  $\text{CdCl}_2$  treatment (namely very high purity  $\text{CdCl}_2$  with vapor deposition) suppressed the inversion, suggesting that  $\text{CdCl}_2$  treatment can affect the defect structure of the material as well. However, inversion was present in all cells used in this study.

The data in Fig. 2 were obtained with a slit width of 100  $\mu\text{m}$  and a 300 groove/mm grating resulting in both spatial and spectral information. Data were integrated over all photon energies to produce the line scans shown. Though EL shows changes in intensity correlated spatially with the Cu dots, integrated PL intensity shows no correlation with Cu. In

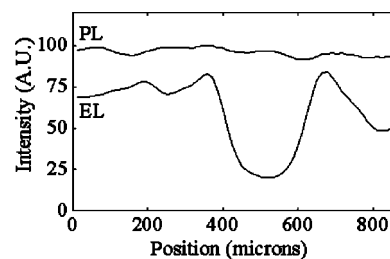


FIG. 2. EL and PL line scans from dashed line indicated in the 70 K EL image in Fig. 1(b). The scans are integrated over photon energy. EL is correlated with the location of Cu whereas PL is not.

other words, EL emission is dominated by Cu doping while integrated PL (to lowest order) is unaffected by Cu. Because EL relies upon electrical injection whereas PL uses direct optical injection, one can conclude that Cu greatly affects conduction through the backcontact to the main diode. At room temperature Cu increases conduction, while at low temperature Cu suppresses conduction, as discussed earlier.

Although emission lines tend to be broad in polycrystalline materials, the spectra presented in Fig. 3 show visible structure. In contrast to the spectrally integrated data above, subtle differences exist in PL between Cu doped and undoped regions. These features are similar in EL and PL and are tentatively identified in the figure based on prior studies, noting that their attribution is not unambiguous. Excitonic structure (X) is observed near the band edge. The most intense feature is a donor–acceptor pair (DAP) band that has been widely reported in other studies.<sup>9–12</sup> Both these features exist in spectra taken from both Cu and non-Cu (undoped) regions. The Cu regions of the cell show increased low-energy emission (toward 1.35 eV) in the DAP band, labeled as  $\text{Cu}_{\text{Cd}}$  related.<sup>11,12</sup> The presence of some Cu-related emission from the undoped region of the cell is not unexpected due to Cu impurities in the CdTe source material. Comparison of the spectral region above the DAP band shows more PL near 1.5 eV in the undoped regions, labeled as  $V_{\text{Cd}}$  related.<sup>12</sup> These small but real differences between the Cu and non-Cu spectra could only be confidently identified us-

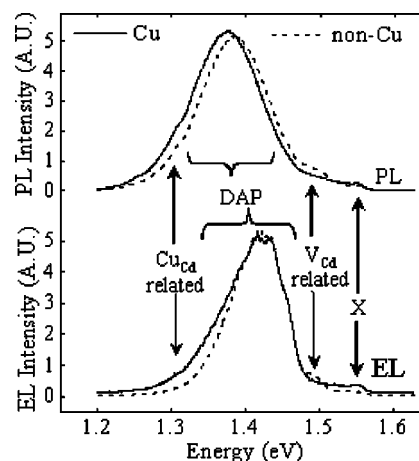


FIG. 3. Spectra from Cu and non-Cu regions. Note separate arbitrary intensity scales for EL and PL. EL intensity from the Cu region was multiplied by three times. PL data are to scale. Features are tentatively identified as band-edge excitonic structure (X), Cd vacancy ( $V_{\text{Cd}}$ ), donor–acceptor-pair (DAP), and emission related to Cu substitutional defects ( $\text{Cu}_{\text{Cd}}$ ). Slight differences between Cu regions and non-Cu regions are visible only because of the techniques used here.  $T = 70$  K.

ing the Cu dot technique along with spatially resolved characterization methods. Seemingly, the presence of Cu affects the concentration of another defect (such as  $V_{\text{Cd}}$  or related complex) in order to incorporate itself into the lattice (as opposed to  $\text{Cu}_i$ , which does not involve replacing another defect), agreeing with the identification of the deep and shallow features as  $\text{Cu}_{\text{Cd}}$  and  $V_{\text{Cd}}$  related, respectively.

By Cu doping CdTe cells in a patterned array, we were able to confirm through a combination of spatially resolved EL and PL measurements that Cu improves performance at least partially by increasing carrier injection (lower  $R_s$ ) through the back of the cell. The EL pattern was found to invert at low temperature suggesting that the presence of Cu must modify another defect in the material that is responsible for transport. Also, our technique allowed us to detect subtle differences in PL and EL spectra between Cu-doped and non-Cu-doped regions. The spectral differences along with the EL inversion at low temperature suggest that, for this process, electrically active Cu incorporates itself into the lattice in the form of  $\text{Cu}_{\text{Cd}}$ , displacing  $V_{\text{Cd}}$  or a related complex.

This material was based on work supported by the Department of Energy under Grant No. ADJ-2-30630-05 and

the National Science Foundation under Grant No. DMR-0103945. The authors wish to thank First Solar, LLC for providing materials for this study.

- <sup>1</sup>A. E. Rakhshani, J. Appl. Phys. **81**, 7988 (1997).
- <sup>2</sup>M. A. Green, K. Emery, D. L. King, S. Igari, and W. Warta, Prog. Photovoltaics **11**, 39 (2003).
- <sup>3</sup>B. E. McCandless and J. R. Sites, in *Handbook of Photovoltaic Science and Engineering*, edited by A. Luque and S. Hegedus (Wiley, West Sussex, England, 2003), p. 633.
- <sup>4</sup>A. S. Gilmore, V. Kaydanov, and T. R. Ohno, Mater. Res. Soc. Symp. Proc. **763**, B9.6.1 (2003).
- <sup>5</sup>T. A. Gessert, M. J. Romero, R. G. Dhere, and S. E. Asher, Mater. Res. Soc. Symp. Proc. **763**, B3.4.1 (2003).
- <sup>6</sup>V. G. Karpov, A. D. Compaan, and D. Shvydka, Appl. Phys. Lett. **80**, 4256 (1999).
- <sup>7</sup>D. Rose, R. Powell, U. Jayamaha, and M. Maltby, *Proceedings of the 29th IEEE PVSC*, 2002, p. 555.
- <sup>8</sup>S.-H. Wei and S. B. Zang, Phys. Rev. B **66**, 155211 (2002).
- <sup>9</sup>D. M. Hofmann, P. Omling, and H. G. Grimmeiss, Phys. Rev. B **45**, 6247 (1992).
- <sup>10</sup>D. Grecu and A. D. Compaan, Appl. Phys. Lett. **75**, 361 (1999).
- <sup>11</sup>M. J. Romero, D. S. Albin, M. M. Al-Jassim, and X. Wu, Appl. Phys. Lett. **81**, 2962 (2002).
- <sup>12</sup>D. Grecu, A. D. Compaan, D. Young, U. Jayamaha, and D. H. Rose, J. Appl. Phys. **88**, 2490 (2000).